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Description

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The present invention relates to optical filter layers for use with ultraviolet radiation (UV) and visible light imageable photosensitive media. In particular, filters are disclosed which absorb in narrow radiation bands and can be easily designed to absorb within the range of 320 to 500 nm to prevent halation in the final image.

A significant problem that has been faced in many forms of imaging technology is termed halation. This image quality diminishing phenomenon is caused by the reflection of actinic radiation which has passed through the radiation sensitive medium and struck a supporting surface in the imageable article. The reflected radiation than passes through the sensitive medium again, imaging the article in a pattern not faithful to the original exposing light pattern. This causes a reduced faithfulness in the final image.

One traditional way of reducing halation is to provide a radiation-absorbing characteristic in the supporting surface. Dye layers, carbon black layers and the like have often been used for this purpose. The use of such radiation-absorbing, anti-halation layers means that the imageable article and often the imaged article will have the color of the radiation-absorbing material of the support surface. Bleachable dyes or strippable layers are often used to allow that undesirable color contribution to be removed. That approach requires considerable manual labor and design expertise to work even moderately well and increases the cost of manufacturing the film by adding layers and coating steps.

It is generally known that ultraviolet (UV) radiation and near ultraviolet (near UV) radiation tend to be the most capable ranges of radiation with respect to halation. The use of titania-filled or coated substrates tends to greatly reduce that problem. Titania provides a clean white background and effectively absorbs much of the radiation below 380 nm. The use of titania still does not solve the problem of near UV halation (i.e., radiation between 390—480). That problem is significant in the reproduction of visible images.

FR—A—1064251 discloses rigid and flexible materials for protecting products e.g. merchandise from the harmful effects of the sun's rays. The materials comprise a synthetic resin and dye. Suitable resins include phenol-formaldehyde resins and suitable dyes include benzylidenes.

US_A-4332116 discloses ultraviolet radiation sensitive photographic materials have a yellow filter dye e.g. a benzylidene coated over the silver halide emulsion.

EP—A—0 029 412 discloses a class of benzylidene dyes suitable for use as antihalation and filter dyes in photographic materials.

It has been found that phenol-formaldehyde resins (both novolaks and resoles) shift the wavelength of maximum radiation absorbance of benzylidene and naphthalamide dyes. Numerous other resins have been tried with these dyes and many other dyes have been tried with phenol-formaldehyde resins, but to date only those unique combinations evidence a significant wavelength shift.

Therefore according to the present invention there is provided an optical transmission filter absorbing radiation between 320 and 500 nm comprising a phenol-formaldehyde resin binder and at least one yellow dye selected from the class of benzylidenes and naphthalimides, comprising a sufficient amount of the phenol-formaldehyde resin to cause a shift in the spectral absorbance of said dye, wherein the dye is represented by the formula:

50 wherein R1 and R2 are independently selected from hydrogen

and electron-withdrawing groups, with the proviso that only one of R¹ and R² may be hydrogen, R³ and R⁴ are independently selected from electron-withdrawing groups, R⁵ is hydrogen, methyl or cyano, R⁶, R², R⁶, Rfl and R¹⁰ are independently hydrogen, alkoxy of 1 to 4 carbon atoms, dialkyl amino (with alkyl groups of 1 to 4 carbon atoms), nitro, or amido, and one pair of adjacent groups may comprise the atoms necessary to form a fused benzene or 5- or 6-membered heterocyclic ring (comprised of only C, N, S, O and H atoms). It is highly desirable to have electron-donating groups on the aromatic ring, particularly in the positions of R⁶, R⁶ and R¹⁰ to influence the strength of absorption and the degree of colour shift. The R⁶ position appears to be the most important for this colour shift.

Strong electron withdrawing groups are preferred for R^1 and R^2 (and for R^3 and R^4) such as CN, $SO_2C_6H_5$, $SO_2C_xF_{2x+1}$ (where x is 1 to 8), and CO_2 -hydrocarbon, where preferably the hydrocarbon is alkyl, aryl, arylalkyl or alkylaryl (e.g., CO_2 -alkyl (1 to 4 carbon atoms in the alkyl)). With very strong electron-withdrawing groups, the remaining R^1 or R^2 group may even be a non-electron-withdrawing group such as phenyl (e.g., tolyl), although that is not preferred.

The naphthalamide dyes have a common nucleus of:

Most of these dyes can be represented by the general structural formula:

wherein R¹¹ is selected from —N, —O, —S or halogen, R¹² is selected from the group consisting of alkyl of 1 to 12 carbon atoms, alkaryl of up to 12 carbon atoms, aryl of up to 10 carbon atoms and arylalkyl of up to 12 carbon atoms, and R¹³ and R¹⁴ are independently selected from the group consisting of hydrogen, alkyl (of 1 to 8 carbon atoms), aryl of up to 10 carbon atoms, and alkaryl of up to 12 carbon atoms (preferably tolyl).

These dyes may be conventionally mixed and dissolved with the polymeric binders and coated onto a release surface to form the filter. The filter layer may also be carried on a transparent substrate and be used in that form as a filter. After removal of the solvent, the dried film is stripped from the release surface and may be used as a filter. The phenol-formaldehyde resin may be used as 100% of the polymeric resin of the film, or may be used in smaller portions in combination with any other binder that is compatible (does not separate or cloud) with the phenol-formaldehyde resin. As smaller amounts of phenol-formaldehyde resin are used, the amount of the chromatic shift decreases. The chromatic shift in the maximum absorption of the dyes by the phenol-formaldehyde resins is always towards the red. That is, the wavelength of the \text{\text{Amax}} increases with increasingly effective amounts of the phenol-formaldehyde resin. The degree of the shift may vary with individual dyes within the classes of benzylidenes and naphthalimides. Some dyes may shift only a few nm when going from 0% to 100% phenolformaldehyde resin while others may shift 30 to 40 nm.

Any compatible resin may be used in combination with the phenol-formaldehyde resin. Amongst the preferred resins are polyvinylacetals (polyvinyl butyral and polyvinyl formal), polyethylene terephthalate, acrylic polymers and copolymers (polymethylmethacrylate), methylacrylate/methylmethacrylate copolymers, etc.), polystyrene, phenoxy resins, vinyl resins and copolymers (polyvinylidene chloride, vinyl chloride/vinyl acetate copolymers) and the like. The film should have structural integrity and should be greater than 1 mil (25,4 µm) in thickness as a single layer construction. It, of course, may be much thinner as a coating on a transparent substrate as long as it provides the desired transmission optical density. Preferably, the film is greater than 2 mils (51 µm) and usually is in the range of 5—20 mils (127—508 µm), although thicker films provide no real disadvantage. The dye containing layers may also be coated onto a transparent carrier or support layers to provide structural integrity. The dye should be present in an amount sufficient to provide a transmission optical density of at least 0.5 at the wavelength of the maximum absorption for the dye. Preferably the concentration of the dye will provide an optical density of greater than 0.8 or greater than 1.0. This may require a concentration of dye of from 0.2 to 15% by weight of the binder, depending upon the thickness of the film.

These and other aspects of the invention are shown in the following non-limiting examples:

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Example 1

The two following solutions were prepared to show the chromatic shift of dyes according to the present invention:

,	SOLUTION A (grams)	SOLUTION B (grams)	INGREDIENTS
10	9.0	0.0	modified resinox, the reaction product of Resinox RS7280 and DD1—1410 diisocyanate,
15			as a 29.2% solids in methyl ethyl ketone solution
20	0.0	9.0	polyvinyl butyral (Butvar B-76)
	0.30	0.30	dispersed Yellow dye 31
25	20.7	27.0	Additional methyl ethyl ketone

The solutions were coated onto a 2-mil (51 μ m) thick transparent polyester film with a #10 Meyer bar and dried at 190°F (88°C) for two minutes. The film produced with Solution A had an absorbance maximum at 452.8 nm, while the film from Solution B has an absorbance maximum at 424.5 nm. The shape of the absorption curves for both coatings remained approximately uniform. This enables the filter to maintain a narrow range of absorption without skewing or shifting at the toe or tail of the absorption curve. The uniformity in the shape of both the peak and the width of the base was maintained.

Example 2

This example describes a large-scale preparation of a specific filter and its use as an effective antihalation tool. The following coating solution was prepared:

45	Dispersed Yellow Dye 31	60 g
45	Butvar B-76 of Example 1	108 g
	Modified Resinox	1440 g
50 .	Additional MEK	1720 a

This solution was reverse roll coated onto 2-mil (51 µm) thick photograde transparent polyester film to various optical densities, and dried at 190°F (88°C). The resulting films had absorbance maxima at 447 nm. This was desired since previous experimentation had shown that a filter with this asborbance would have an optimal antihalation effect on 3M Positive Matchprint. Samples of cyan Positive Matchprint, after lamination onto a titanium dioxide-coated support, were exposed using a 5 KW diazo lamp as the UV light source through these filters, and subsequently processed with an aqueous alkaline developer. The samples exposed through the filters had substantially better image quality with little halation, especially at longer exposure times. The more dense the yellow filter was made, the greater the effect on resolution and exposure latitute became.

Example 3

Each of the following dyes were used in these Examples. Five separate coating solutions were prepared for each dye. The coating solutions each consisted of dye, the modified Resinox of Example 1 and

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polyvinyl butyral. The composition of the individual solutions was as follows in weight percent of the dry film:

SOLUTION	DYE	RESINOX	POLYVINYL BUTYRAL
Α	10	90	0
В	10	72	18
С	10	45	45
D	10	18	72
Е	10	0	90

The dyes used in the Examples had the structural formulae:

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After coating and drying of these solutions onto a 2-mil (51 μm) transparent polyester substrate, the following data were obtained:

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SOLUTION B SC AWY AMAX A AWY AMAX	SOLUTION B A AW'S AMAX	ушух з	ушу з	ушах	* 1	SOLUTION C	C C AWS	SO	SOLUTION D	1 D AWS	SO	SOLUTION E	AWS
64		448.2	2.3	64	438.0	2.1	99	428.0	2.6	99	424.5	1.1	62
57 449	44	449.0	2.27	58	440.3	3.16	28	431.7	5.6	28	424.1	1.9	28
56 444.0	444	0.	2.55	26	436.5	2.16	26	428.6	2.04	95	421.3	2.65	09
73 451.9	451	6.	2.05	69	445.8	2.7	70	439.4	2.63	28	436.3	2.62	65
74 460.8	460	æ	1.48	89	457.3	1.73	63	453.1	2.71	25	448.9	1.68	19
379.0	379.	0	1.98	104	377.8	.80	102	376.2	.97	96	376.3	.86	94
<320	<320				<320			<320			< 320		
54 439.1	439.1		1.22	53	437.2	1.42	58	434.1	1.05	29	429.8	2.23	63
62 357.4	357.4		2.14	52	350.0	2.92	52	340.2	1.16	23	335.5	2.64	48
94 488.2	488.2		1.07	88	476.5	1.27	88	465.0	2.16	82	459.4	1.41	78
66 410.1	410.1		<i>H</i> .	64	408.5	1.62	09	405.6	5.06	28	402.5	1.75	26
70 393.4	393.4		.74	70	389.1	.85	89	384.4	17.	65	383.8	.72	64
82 381.2	381.2		2.44	82	375.8	1.18	80	373.3	1.66	92	370.9	2.24	02
86 379.6	379.6		.50	82	375.0	.52	84	369.2	1.04	74	368.1	.54	72
84 369.0	369.		.34	82	368.0	.43	82	361.8	.26	80	362.9	.47	20
64 382.9	382.9	_	.90	62	377.4	1.05	09	372.7	1.66	25	369.7	2.27	23
82 372.4	372.4	_	.61	78	368.8	.64	77	366.3	1.16	20	364.1	.88	74

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ш	4WA	29	84	64	90	88	64				70	64	75	69	78		72	68	72
SOLUTION E	A	2.14	.49	2.13	3.26	.63	2.09				1.88	1.69	.57	.40	.67	3.6	1.56	.41	.23
	у шах	365.8	402.9	350.0	336.3	353.9	357.9	<320	<320	< 320	350.0	386.8	431.0	427.0	425.4	344.6	337.1	431.1	429.4
SOLUTION D	AW'S	9	84	99	94	88	99				20	99	78	20	78			69	1,1
	A	1.31	.47	1.65	1.75	.68	1.75				1.46	1.85	.68	.65	.45	3.4	.75	.45	.36
SS	у шах	367.8	406.0	354.4	337.6	355.5	361.2	<320	<320	<320	350.0	388.2	438.5	433.8	426.9	348.0	338.4	435.5	433.8
SOLUTION C	AW.	99	96	20	94	90	69				77	89	τί	89	78	73	72	99	72
	A	.91	.34	1.09	2.3	.65	1.01				.68	1.70	96.	.40	.74	2.17	1.28	.41	.38
SOLI	хвм γ	372.3	410.2	356.8	340.8	357.2	367.1	< 320	. < 320	<320	350.0	392.9	444.6	441.5	435.0	350.0	350.0	443.4	439.9
ш	ΔWλ	7.1	90	73	100	96	69				84	92	78	89	80	78	78	65	70
SOLUTION B	4	.82	.42	1.29	1.15	.68	1.12			.95	. 55	1.15	.53	.43	.47	1.19	.68	.30	.36
SOI	ушах	377.2	415.2	359.2	342.9	359.0	373.7	<320	< 320	330.9	350.0	397.5	450.4	446.5	436.6	355.0	350.0	451.8	444.9
_	A57.	73	94	75	112	98	89				78	72	76	99	74	84	78	99	0,
SOLUTION A	4	.78	.37	.93	1.21	.78	1.16			.97	1.09	69.	.51	.39	.55	2.8	99.	.32	.28
TOS	у шах	380.8	416.5	360.4	350.0	362.1	379.3	<320	<320	337.2	355.7	400.8	453.6	447.7	437.1	360.9	350.0	451.8	448.2
EXE EXE		2	77	22	23	24	25	56	27	58	53	30	31	32	33	34	35	36	37

Claims

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1. An optical transmission filter absorbing radiation between 320 and 500 nm comprising a phenolformaldehyde resin binder and at least one yellow dye selected from the class of benzylidenes and naphthalamides, comprising a sufficient amount of the phenol-formaldehyde resin to cause a shift in the spectral absorbance of said dye, wherein the dye is represented by the formula:

in which:

R1 and R2 independently represent hydrogen, an electron-withdrawing group or

with the proviso that no more than one of R1 and R2 are hydrogen,

R3 and R4 independently represent electron-withdrawing groups,

R⁵ represents hydrogen, methyl or cyano, and

R⁶, R⁷, R⁸ and R¹⁰ independently represent hydrogen, alkoxy of 1 to 4 carbon atoms, dialkyl amino in which the alkyl groups contain 1 to 4 carbon atoms, nitro, or amido, or one pair of groups adjacent on the benzene ring may comprise the atoms necessary to form a fused benzene ring or 5- or 6-membered heterocyclic ring comprised of only C, S, N and O ring atoms.

2. A filter as claimed in Claim 1 characterised in that at least one of R⁶, R⁸ and R¹⁰ are electron-donating

3. A filter as claimed in Claim 1 or Claim 2 characterised in that R¹ and R² are both strong electron-withdrawing groups selected from CN, CO₂R in which R is a hydrocarbon group of 1 to 12 carbon atoms, SO₂C₅H₅ and SO₂CѫF₂₂₊₁ in which x is 1 to 8.

4. A filter as claimed in any preceding claim characterised in that R⁸ comprises a dialkyl amino.

5. A filter as claimed in any preceding claim characterised in that at least one of R¹ and R² is cyano and the other is an electron-withdrawing group.

6. A filter as claimed in any preceding claim characterised in that the phenol-formaldehyde resin comprises from 20 to 100% by weight of the binder.

7. A filter as claimed in Claim 1 characterised in that the nucleus of said at least one dye is represented by either of the formulae:

in which:

R¹¹ represents halogen and

R¹² represents an alkyl groups of 1 to 12 carbon atoms or alkaryl groups of 1 to 12 carbon atoms, an aryl groups of up to 10 carbon atoms, or an arylalkyl group of up to 12 carbon atoms, or

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in which:

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 R^{12} represents an alkyl group of 1 to 12 carbon atoms, an alkaryl groups of 1 to 12 carbon atoms, an aryl group of up to 10 carbon atoms, or an arylalkyl of up to 12 carbon atoms, and

 R^{13} and R^{14} independently represent hydrogen atoms, an alkyl group of 1 to 4 carbon atoms, an arylinear state of the state o group of up to 10 carbon atoms or an alkaryl group of up to 12 carbon atoms.

Patentansprüche

1. Strahlung zwischen 320 und 500 nm absorbierendes Lichttransmissionsfilter, umfassend ein Phenol-Formaldehyd-Harz-Bindemittel und mindestens eine gelben Farbstoff aus der Gruppe der Benzylidene und Naphthalimide mit einer ausreichenden Menge des Phenol-Formaldehyd-Harzes, um eine Verschiebung der spektralen Absorption des Farbstoffes zu verursachen, wobei der Farbstoff durch die Formel

wiedergegeben wird, in der:

R¹ und R² unabhängig voneinander Wasserstoffatome, einen Elektronen-ziehenden Rest oder den Rest der Formel

darstellen, mit der Maßgabe, daß höchstens einer der Reste R¹ und R² ein Wasserstoffatom ist, R³ und R⁴ unabhängig voneinander Elektronen-ziehende Reste bedeuten,

R⁵ ein Wasserstoffatom, eine Methyl- oder Cyanogruppe darstellt und R⁶, R⁷, R⁸, R⁹ und R¹⁰ unabhängig voneinander Wasserstoffatome, Alkoxyreste mit 1 bis 4 Kohlenstoffatomen, Dialkylaminoreste, in denen die Alkylreste 1 bis 4 Kohlenstoffatome enthalten, Nitrooder Amidogruppen bedeuten, oder ein am Benzolring benachbartes Restepaar, die zur Erzeugung eines kondensierten Benzolringes oder eines nur aus C, S, N und O-Ringatomen bestehenden 5- oder 6gliedrigen heterocyclischen Rings erforderlichen Atome umfassen kann.

2. Filter nach Anspruch 1, dadurch gekennzeichnet, daß mindestens einer der Reste R6, R6 und R10 ein Elektronenlieferner Rest ist.

3. Filter nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß R1 und R2 beide stark Elektronen-ziehende Reste darstellen, nämlich —CN—CO₂R, wobei R einen Kohlenwasserstoffrest mit 1 bis 12 Kohlenstoffatomen bedeutet, -SO₂C₅H₆ oder SO₂C_xF_{2x+1}, wobei x einen Wert von 1 bis 8 hat.

4. Filter nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß R^s einen Dialkylaminorest umfaßt.

5. Filter nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß mindestens einer der Reste R1 und R2 eine Cyanogruppe und der andere ein Elektronen-ziehender Rest ist.

6. Filter nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß das Phenol-Formaldehyd-Harz 20 bis 100 Gew.-% des Bindemittels umfaßt.

7. Filter nach Anspruch 1, dadurch gekennzeichnet, daß der Kern des mindestens einen Farbstoffes durch eine der Formeln dargestellt wird:

in der:

R11 ein Halgenatom bedeutet und

R¹² einen Alkylrest mit 1 bis 12 Kohlenstoffatomen oder einen Alkarylrest mit 1 bis 12

Kohlenstoffatomen, einen Arylrest mit bis zu 10 Kohlenstoffatomen oder einen Arylalkylrest mit bis zu 12 Kohlenstoffatomen darstellt, oder

in der:

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R¹² einen Alkylrest mit 1 bis 12 Kohlenstoffatomen, einen Alkarylrest mit 1 bis 12 Kohlenstoffatomen, einen Arylrest mit bis zu 10 Kohlenstoffatomen oder einen Arylalkylrest mit bis zu 12 Kohlenstoffatomen bedeutet, und R¹³ und R¹⁴ unabhängig voneinander Wasserstoffatome, einen Alkylrest mit 1 bis 4 Kohlenstoffatomen, einen Arylrest mit bis zu 10 Kohlenstoffatomen oder einen Alkarylrest mit bis zu 12 Kohlenstoffatomen bedeuten.

20 Revendications

1. Filtre de transmission optique absorbant les radiations entre 320 et 500 nm, comprenant un liant du type résine à base de phénol-formaldéhyde et au moins un colorant jaune choisi parmi la classe des benzylidènes et des naphtalimides, comprenant une quantité de résine à base de phénol-formaldéhyde suffisante pour provoquer un déplacement de l'absorption spectrale dudit colorant, dans lequel le colorant est répresenté par la formule

dans laquelle

R¹ et R², indépendamment l'un de l'autre, représentent chacun un hydrogène, un groupe attracteur d'électrons ou

à la condition que pas plus d'un des radicaux R1 et R2 soit un hydrogène,

R3 et R4, indepéndamment l'un de l'autre, représentent chacun un groupe attracteur d'électrons,

R⁵ représente un hydrogène ou le radical méthyle ou cyano, et

R⁶, R⁷, R⁸ et R¹⁰, indépendamment les uns des autres, représentent chacun un hydrogène, un radical alcoxy ayant de 1 à 4 atomes de carbone, dialkylamino dans lequel les groupes alkyle contiennent de 1 à 4 atomes de carbone, nitro ou amido, ou encore deux groupes immédiatement voisins du noyau benzénique peuvent comprendre les atomes nécessaires à la formation d'un noyau benzénique condensé ou d'un noyau hétérocyclique ayant de 5 à 6 sommets et constitué uniquement d'atomes C, S, N et O.

2. Filtre selon la revendication 1, caractérisé en ce qu'au moins l'un des radicaux R⁶, R⁸ et R¹⁰ est un groupe donneur d'électrons.

3. Filtre selon la revendication 1 ou la revendication 2, caractérisé en ce que R¹ et R² sont tous les deux des groupes fortement attracteurs d'électrons choisis parmi CN, CO₂R où R est un groupe hydrocarboné ayant de 1 à 12 atomes de carbone, SO₂C₀H₅ et SO₂C₂F₂x₊₁ où x vaut de 1 à 8.

4. Filtre selon l'une quelconque des revendications précédentes, caractérisé en ce que R⁸ est un radical dialkylamino.

5. Filtre selon l'une quelconque des revendications précédentes, caractérisé en ce qu'au moins l'un des groupes R¹ et R² est le radical cyano, et l'autre est un groupe attracteur d'électrons.

6. Filtre selon l'une quelconque des revendications précédentes, caractérisé en ce que la résine à base de phénol-formaldéhyde compte pour 20 à 100% en poids du liant.

7. Filtre selon la revendication 1, caractérisé en ce que le noyau d'au moins un desdits colorants est représenté par l'une des formules suivantes:

dans laquelle

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R¹¹ représente un halogène et

R¹² représente un groupe alkyle ayant de 1 à 12 atomes de carbone, ou un groupe alcaryle ayant de 1 à 12 atomes de carbone, un groupe aryle ayant jusqu'à 10 atomes de carbone ou un groupe arylalkyle ayant jusqu'à 12 atomes de carbone, ou bien

$$\begin{array}{c|c}
R^{13} & & & \\
R^{14} & & & \\
\end{array}$$
N-R¹²

25 dans laquelle:

R¹² représente un groupe alkyle ayant de 1 à 12 atomes de carbone, un groupe alcaryle ayant de 1 à 12 atomes de carbone, un groupe aryle ayant jusqu'à 10 atomes de carbone, ou un groupe arylalkyle ayant jusqu'à 12 atomes de carbone, et

R¹³ et R¹⁴, indépendamment l'un de l'autre, représentent chacun un atome d'hydrogène, un groupe alkyle ayant de 1 à 4 atomes de carbone, un groupe aryle ayant jusqu'à 10 atomes de carbone ou un groupe alcaryle ayant jusqu'à 12 atomes de carbone.